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Sixth Quarterly Progress Report
December 1963 and January, February 1964

to

Aeronautical Systems Division
Wright Patterson Air Force Base
Ohio

FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

F. Tepper
J. Greer

16 March 1964

MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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⑤ 238400 MSA Research Corp.,
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⑥ FACTORS AFFECTING THE COMPATIBILITY OF
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①② by F. Tepper and
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MSA RESEARCH CORPORATION
Callery, Pennsylvania

4711

G.C.

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ABSTRACT

Y Tests with the dissimilar metal couples TD-Nickel vs Nb-1%Zr, TD-Nickel vs Mo-1/2%Ti and Nb-1%Zr vs Mo-1/2%Ti have continued with metallographic, chemical and also microprobe analyses. Solubility studies on the refractory alloys Nb-1%Zr and Mo-1/2%Ti have indicated that the solubilities of the major constituents are approximately 20 ppm and that there are possible synergistic effects resulting from the presence of the alloying elements. Capsules fabricated from Haynes-25 alloy and TD-Nickel have shown (relatively little attack upon exposure to refluxing cesium) at 1800°F and Mo-1/2%Ti alloy has survived a 255 hr test at 2500°F showing some dissolution of the alloy in the boiling liquid cesium ↗

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MSA Research Corporation

Sixth Quarterly Report
on
FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

F. Tepper
J. Greer

INTRODUCTION

This is the sixth quarterly progress report on a program directed at the determination of mechanisms of corrosion on selected structural materials by cesium. Progress to date has been directed at the following avenues of investigation:

1. Determination of the transfer of metallic species through liquid cesium in dissimilar metal couples which are exposed under isothermal conditions.
2. Attempts to determine equilibrium solubility of species in liquid cesium have been made.
3. Boiling-refluxing capsule tests have been initiated.
4. Determination of the solubility of carbon in cesium has been initiated. Interaction between carbon and oxygen in liquid cesium is also being studied.

DISSIMILAR METAL STUDIES

TD-Nickel vs Nb-1%Zr and Mo-1/2%Ti

One capsule fabricated from TD-Nickel which included a Nb-1%Zr tab immersed in liquid cesium was exposed 500 hrs at 1800°F. Metallography associated with this test has been reported in a previous quarterly. The TD-Nickel capsule was sectioned and analysed with the electron microprobe to determine the mode of mass

transfer of niobium to the nickel interface and into the matrix of the nickel alloy. Figure 1 is the niobium-reflected electron pattern from the TD nickel surface, while Figure 2 is a plot of the niobium concentration as a function of distance from the surface. A zone approximately 35 microns deep on the inside surface of the capsule was found to contain 25.3 wt % niobium, which is close to the peritectic composition reported by Hansen¹ of 23.5 wt % niobium. The niobium concentration falls precipitously between 30 and 60 microns, after which there is a gradual decrease of the niobium concentration. The profile is plotted down to 1 wt % niobium (to 300 microns) at which point the niobium content is below the precision of the microprobe. The data shown in Figure 2 suggests that the rate determining mechanism in the transfer of niobium is the diffusion of niobium through the TD-Nickel matrix.

The transfer of nickel to the niobium tab was found to be slight. In fact, there was an 11% wt loss in the tab as the result of exposure during the test, indicating a net transfer of niobium to nickel.

A dissimilar metal test was performed where a Mo-1/2Ti tab was inserted into a TD-Nickel capsule. After 273 hours of operation at 1800°F with liquid cesium, a leak developed in the Hastalloy-W weld area and the test was discontinued. The surface of the TD nickel capsule which had been exposed to liquid cesium is shown in Figure 3. A molybdenum bearing coating approximately 45 microns thick was formed on the nickel only in that section exposed to liquid cesium. The Mo-1/2Ti tab contained in this capsule experienced a 7.6% wt loss during this test. A net transfer of molybdenum to the nickel surface was indicated, and the test is to be duplicated with an exposure time of 500 hours. Thus, it is hoped that relative transfer rates of niobium from Nb-1%Zr and molybdenum from Mo-1/2Ti can be compared.

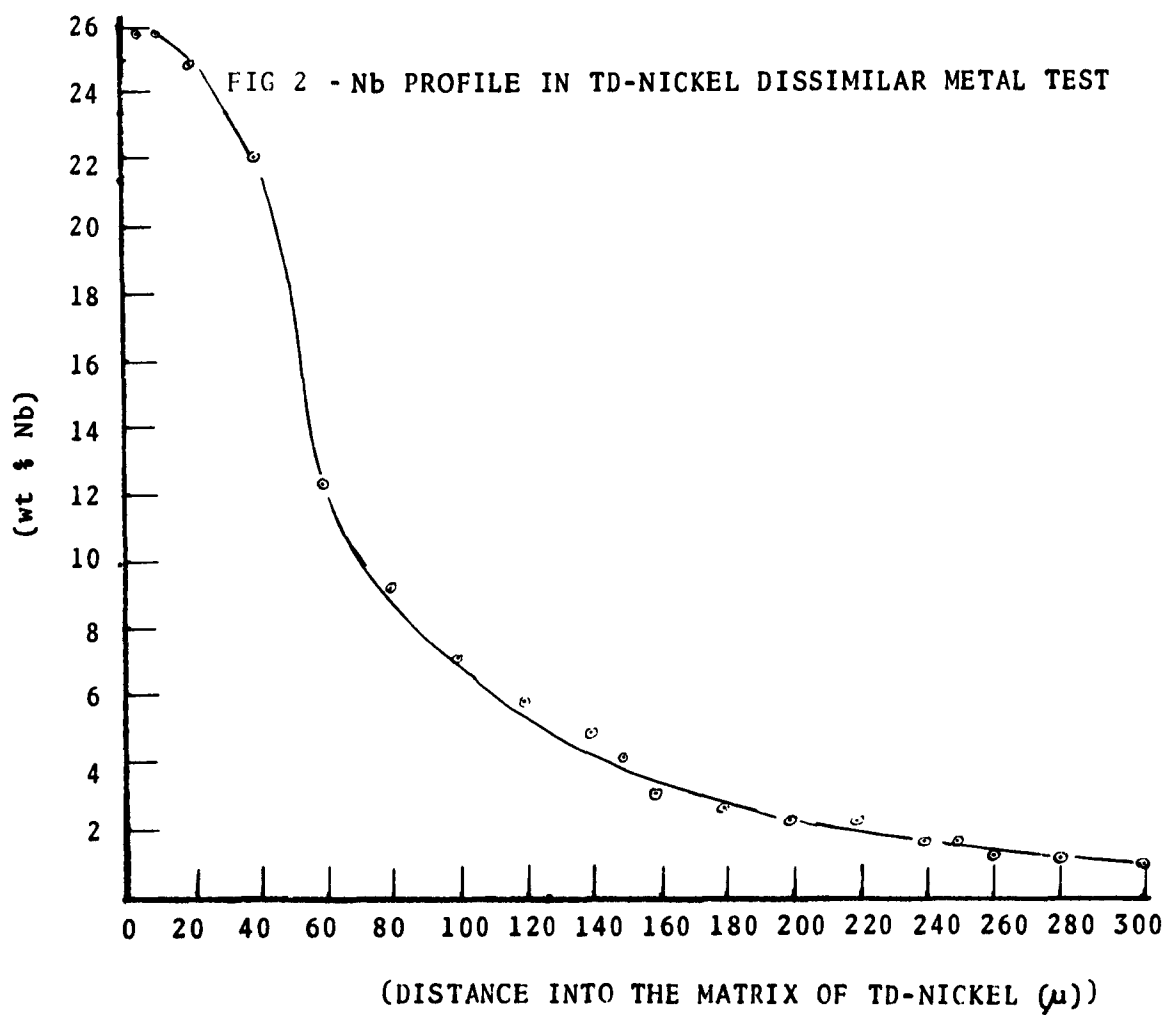
Nb-1%Zr vs Mo-1/2Ti

A dissimilar metal test was performed where the components were a Nb-1%Zr capsule and a Mo-1/2Ti tab. The cesium which was charged in the capsule contained an oxygen spike equivalent to 100 ppm oxygen. The capsule was exposed to a temperature of 2500°F for 100 hours. The corrosion data from this capsule test was compared to that of a similar test, where no Mo-1/2Ti insert was included.

1. Hansen, Max, Constitution of Binary Alloys, pp 1010-1012.



FIG 1 - Nb BACK SCATTERING FROM TD-NICKEL SURFACE
(280 μ^2 area)



The post-test surface of the Nb-1%Zr capsule is shown in Figure 4. While no foreign surface phase appears to have formed, hardness measurements indicated enrichment of the surface by either molybdenum or oxygen. Intergranular penetration and precipitation of a foreign phase is seen throughout the structure. This phase is thought to be an oxide of zirconium.

Microprobe analysis of this particular couple is underway, with the results to be reported in the next quarterly.

SOLUBILITY STUDIES

Table 1 shows the results of equilibrium solubility tests performed where the solutes are Mo-1/2Ti and Nb-1Zr alloys. These tests were similar to the tip capsule tests performed earlier in the program, with the exception that a refractory metal alloy was utilized as the "catch" crucible. Analysis of trace metals in the cesium sample contained by the crucible after test was performed by emission spectrographic analysis. The analyses of the respective tests are listed in Table 1 in the order of decreasing exposure times.

Samples taken in Mo-1/2Ti solubility capsules having equilibration times between 100 hrs and 5 minutes indicate molybdenum values at approximately 20 ppm. The results suggests that the solubility of molybdenum in cesium at 2500°F is approximately 20 ppm, and that equilibration time is rapid. Indeed, using the present technique, it would appear that equilibration occurs with such rapidity that the heat up time masks the data, precluding the possibility of deriving kinetics at this temperature. Examination of the titanium values suggests a possible increase of titanium content in the melt with time. It is suspected that true equilibrium has not been obtained in that titanium may have a synergistic effect on the solubility of molybdenum.

Solubility data with Nb-1%Zr alloy again shows an "equilibrium solubility" of the order of 20 ppm, and kinetics associated with the attainment of this quasi-equilibrium appears to be similar to that observed with Mo-1/2Ti. The emission spectrophic results obtained with samples taken in refractory metal crucibles show somewhat better precision than those obtained with samples taken in high purity alumina crucibles in the past.

Solubility studies are to be curtailed for the near future. The experimental solubility studies performed to date result in the following conclusions:

1. Synergistic solubility effects appear to exist between the two structural metal components of an alloy in the liquid cesium.

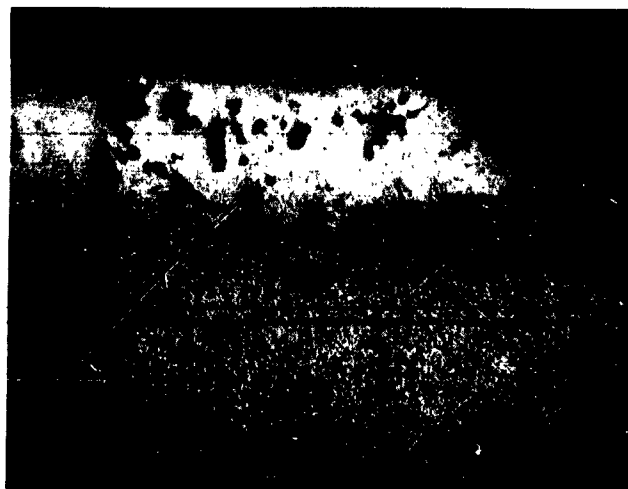


FIG 3- TD-NICKEL EXPOSED 273 HRS TO LIQUID CESIUM
AT 1800°F ALONG WITH A Mo-1/2%Ti TAB
Etchant: Aqua regia 266X



FIG 4 - Nb-1%Zr CAPSULE EXPOSED 100 HRS AT 2500°F
TO CESIUM CONTAINING AN O₂ ADDITION
Etchant: duPont's etchant 266X

TABLE 1 - SOLUBILITY ANALYSES FOR REFRACTORY ALLOYS

Capsule	1	2	3	4	5	1	2	3	4	5	Nb-1Zr	Nb-1Zr	Nb-1Zr	Nb-1Zr	Nb-1Zr
Equilibration Time	100 hrs	100 hrs	14 hrs	45 min	5 min	100 hrs	40 hrs	20 hrs	10 hrs	5 min					
Sampling Crucible	Nb-1Zr	Nb-1Zr	Nb-1Zr	Nb-1Zr	Nb-1Zr	Nb-1Zr	Mo-1/2Ti Mo-1/2Ti	Mo-1/2Ti Mo-1/2Ti	Mo-1/2Ti Mo-1/2Ti	Mo-1/2Ti Mo-1/2Ti					
Metallic Content (ppm)															
Niobium	--	--	--	--	--	30	<10	10	20	10					
Molybdenum	10	10	25	90	10	--	--	--	--	--					
Zirconium	--	--	--	--	--	10	<10	10	10	10					
Titanium	<5	150	100	<5	<5	--	--	--	--	--					

This appears to be primarily the case in the Mo-Ti alloy studies. Future solubility studies will be performed solely on the pure elements.

2. The solubility of the refractory metal species molybdenum and columbium in cesium appear to be approximately 10-20 ppm at 2500°F. Since such order of solubility exists at 2500°F, where the level of solubility is near the detectable limit of emission analysis, solubility studies with these metals, if performed in the present program, will only be performed at a minimum temperature of 2500°F.
3. The tip capsule technique that has been utilized to date does not appear to result in kinetic data associated with the attainment of equilibrium. The time (6-8 hrs) necessary for heating a capsule to 2500°F is apparently responsible for the inability to derive kinetic data.
4. Better precision is attained when oxides such as alumina are not present in the system. The wide degree of scatter obtained when alumina crucibles were used suggests sufficient interaction of the cesium and/or the refractory metal with alumina to cloud solubility results.

BOILING-REFLUXING TESTS

Haynes-25

A Haynes-25 capsule which has been exposed to boiling-refluxing cesium for 500 hrs (see Fifth Quarterly Report) has shown minimal corrosion effects. Only slight variations of the carbon and nitrogen concentrations were found to have resulted from exposure to refluxing cesium. The oxygen concentration of the alloy exposed to the boiling liquid metal increased by a factor of 6 while that exposed to the condensate decreased slightly. A second Haynes-25 reflux capsule is under test at 1800°F for a planned 1000 hrs.

TD-Nickel

Two capsules of TD-nickel have been exposed to refluxing cesium for respective times of 260 and 500 hrs. The surface of the nickel exposed to the liquid cesium in the 260 hr test is

shown in Figure 5 while that of the 500 hr test is shown in Figure 6. Both capsules experienced no changes in macrohardness as a result of exposure to the boiling cesium. No macrohardness variation was noted traversing the exposed surface from the liquid to the condensing region. A longitudinal section of the TD-nickel capsule which had undergone 500 hrs of test is shown in Figure 7. The portion to the left which had been exposed to the liquid shows the relative absence of machining grooves as compared to the condensing portion to the right. Each of the two capsules showed nickel crystallite formation at the bottom of the capsule.

Chemical analysis are presently being performed on sections from each of the two TD-nickel reflux tests. It is hoped that such analyses will indicate the possible nature of the corrosion layer seen in the photomicrographs seen in Figures 5 and 6.

Mo-1/2Ti

A Mo-1/2Ti capsule was exposed to refluxing cesium (2500°F) for 255 hrs. The capsule (3/4 in. OD x 1/8 in. wall x 8 1/2 in. high) had been filled with approximately 8 grams of cesium and was sealed by electron beam welding. Figure 8 is an oblique view of the capsule after test. The condensing section is in the foreground with the boiling section in the rear. Crystallites have accumulated in a narrow region that represents the liquid vapor interface. The narrow region in which these crystallites have formed suggests that stable boiling had occurred. Little if any spattering and accumulation of molybdenum in the condensing region appears to have occurred. Machining grooves still remain in the condensing section, while the alloy exposed to the liquid region has attained a highly polished surface.

Semi-quantitative analysis of a sample of the crystallites that had accumulated at the liquid-vapor interface was performed and the titanium composition of the molybdenum crystallites was found to be approximately 1/2%, the composition of the "as-received" alloy. Quantitative analysis of these crystallites is in progress. Figures 9 and 10 are photomicrographs of the region exposed to the liquid while the region exposed to the vapor is shown in Figure 11. Uniform dissolution of the molybdenum alloy is apparent, and is accompanied by grain growth at the surface. Some degree of grain growth was also evidenced in a section exposed to the vapor, although grain growth is not as extensive in this region.

Analyses of the carbon, nitrogen and oxygen contents in the Mo-1/2Ti exposed to the boiling liquid, condensing vapor, and also the section at the interface of the two cesium phases have shown definite trends in the diffusion and scavenging of the non-



FIG 5 - TD-NICKEL CAPSULE EXPOSED 260 HRS AT
1800°F TO BOILING CESIUM

Etchant: Aqua regia

266X



FIG 6 - TD-NICKEL CAPSULE EXPOSED 500 HRS AT
1800°F TO BOILING CESIUM

Etchant: Aqua regia

266X

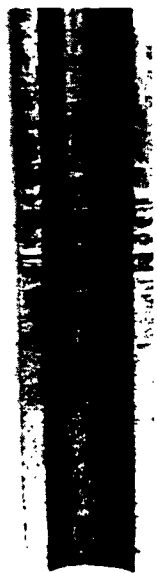


FIG 7 - TD-NICKEL CAPSULE EXPOSED
500 HRS AT 1800°F TO REFLUXING CESIUM
(The area to the left where
machining cuts have been re-
moved was exposed to liquid
cesium)

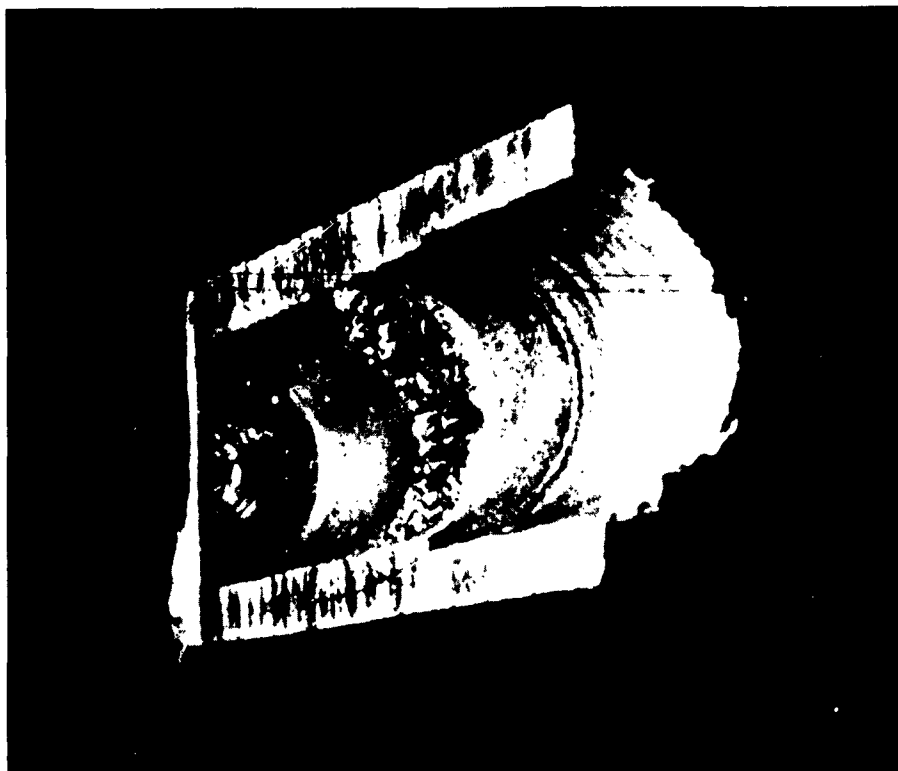


FIG 8 - Mo-1/2%Ti CAPSULE EXPOSED 255 HRS AT
2500°F TO REFLUXING CESIUM
(The crystals were formed at the top of the
liquid at test temperature and extend approxi-
mately 4 mm from the wall)

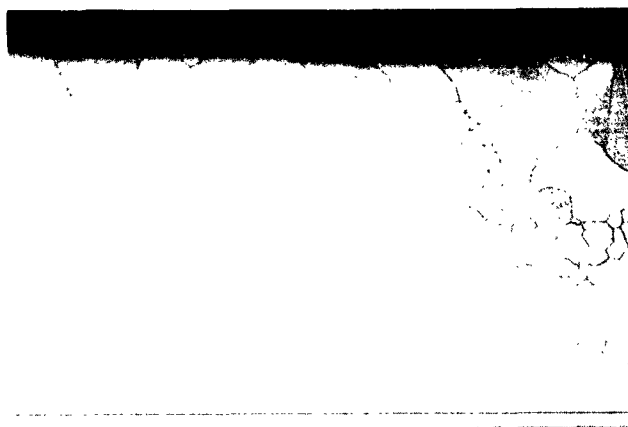


FIG 9 - Mo-1/2%Ti CAPSULE EXPOSED
255 HRS AT 2500°F
TO BOILING CESIUM
Etchant: Murakami's reagent 133X



FIG 10- Mo-1/2%Ti CAPSULE EXPOSED
255 HRS AT 2500°F
TO BOILING CESIUM
Etchant: Murakami's reagent 266X

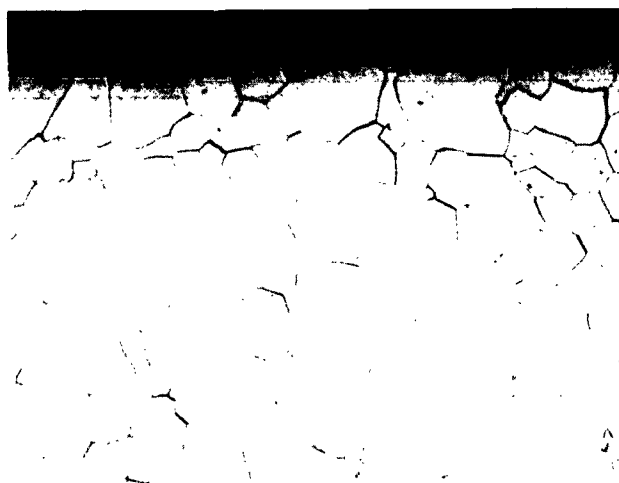


FIG 11- Mo-1/2%Ti CAPSULE EXPOSED
255 HRS AT 2000°F
CONDENSING CESIUM
Etchant: Murakami's reagent 266X

metallics within the system. Decarburization of the Mo-1/2Ti took place throughout the capsule but was greatest in the section exposed to cesium vapor (-140 ppm). Very little decarburization occurred at the interface (-50 ppm), while that in the areas exposed to boiling liquid was intermediate (-100 ppm).

Increases in nitrogen content also showed a definite trend traversing the capsule. The section exposed to boiling cesium increased 180 ppm and larger concentrations were found at the interface and in the section exposed to vapor.

Mo-1/2Ti has consistently shown a greater ability to scavenge oxygen from the liquid phase. In this capsule the oxygen concentration of the alloy increased 300 ppm in the section exposed to boiling cesium while both the other sections analyzed gained approximately 100 ppm. The sample taken from the interface section showed the least gain in carbon and oxygen.

Nb-1Zr

One Nb-1Zr reflux capsule test was performed during this report period. After 10 hrs of exposure to condensing cesium at 2500°F, failure occurred in the weld area. Failure of this capsule resulted in the reaction of the escaping cesium with the mullite vacuum tube. Rupture of the vacuum tube occurred and this capsule was too extensively oxidized to permit evaluation of the cause of failure. Future Nb-1Zr reflux tests are planned at temperatures between 2000 and 2200°F.

Reflux tests are planned with a tantalum base alloy (FS-60) and a niobium base alloy (FS-85) with high temperature mechanical properties superior to that of Nb-1Zr.

DETERMINATION OF THE SOLUBILITY OF CARBON IN CESIUM

The initial carbon concentration of as produced 99.9+% cesium has been established and investigation was undertaken of the variations of carbon content with temperature prior to the addition of carbon. Carbon analysis of the cesium in the charge after maintaining it at 270°F was 21 ppm (the average of 4 analysis where the average deviation was 6 ppm). The freezing point of the cesium was measured and was found to be 28.55°C, a value higher than had been observed previously. Sampling of the cesium for carbon value at 800°F was found to be approximately 17 ppm. While the results seem to indicate a decrease in carbon, the apparent reduction is probably a result of improved accuracy. Carbon additions to the cesium melt are to be made within the near future and sampling of saturated cesium is to begin shortly thereafter.